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Inverse Regime of Ionic Modification of Surface Anchoring in Nematic Droplets

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It was found that the effect of the ionic modification of anchoring in liquid-crystal droplets can be implemented in the inverse regime. Droplets of 4-*n*-pentyl-4'-cyanobiphenyl nematic doped with ionic cetyltrimethylammonium bromide surfactant were dispersed in polyvinyl alcohol and investigated. In the initial state, nematic droplets have a radial structure with homogeneous homeotropic anchoring typical of the surfactant used. In the presence of a dc electric field, the boundary conditions become tangential in the surface area left by the cations. That results in the transformation of an orientational structure following by various scenarios. For the new states of nematic droplets, the distribution of the director field was analyzed and the corresponding textural patterns were numerically calculated.

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INTRODUCTION

The study of local Friedericksz transitions [1–4] laid the foundation for new approaches to the control of liquid crystals (LCs). In this case, the director reorientation proceeds due to the action of external forces not on the LC bulk but on the interface through changing the surface anchoring of the LC molecules to the substrate. For practical use, the methods of electrically controlled interfaces are of particular interest. The reorientation of a nematic LC layer through the electrically controlled reconstruction of the boundary conditions was successfully implemented using ferroelectric LC polymers as coatings for the substrates of optical cells [5].

In [6], the ionic surfactant method for modifying the surface anchoring was suggested and implemented by the example of polymer-dispersed LC (PDLC) containing an ion-forming impurity of a surface-active material (surfactant). In the initial state, the orientational structure of the LC droplets was governed by the tangential (planar) anchoring of nematic molecules to the polymer matrix. Under the action of an electric field, the boundary conditions changed to homeotropic (normal) in the droplet surface region where the surface-active ions were concentrated. As a result of such an interface reconstruction, the initially bipolar structure of nematic droplets was transformed to a monopolar.

In this work, the possibility of implementing an inverse regime for the ionic modification of surface anchoring was considered and it was shown that this effect can be observed at a high surfactant concentration.

SAMPLES AND METHODS OF INVESTIGATION

Samples of a PELC film prepared by the LC emulsification in a polymer solution followed by solvent evaporation were studied [7]. For this purpose, a nematic 4-*n*-pentyl-4'-cyanobiphenyl (5CB) and an aqueous solution of polyvinyl alcohol (PVA) plasticized with glycerol (Gl) were used. Cationic surfactant cetyltrimethylammonium bromide (CTAB) was preliminary added to the nematic. The weight ratio 5CB : PVA : Gl : CTAB of the components was 1 : 19 : 6 : 0.1. Note that the surfactant concentration was 10 times higher than in [6].

It is known that the 5CB nematic is aligned tangentially at the surface of polyvinyl alcohol even in the presence of glycerol additions [7]. When dissolved in LC, the surfactant decomposes into bromide ions Br^- and cetyltrimethylammonium ions CTA^+. The bromide ions only have a small effect on the boundary conditions [6]. The CTA^+ ions, being adsorbed on the interface, can form a nanosized layer that governs the homeotropic alignment of the LC molecules at a certain concentration [8].

Samples of the composite films ~30 μm in thickness were placed on a glass substrate with electrodes allowing a dc electric field to be applied along the film plane. The average size of the LC droplets was equal to 7–11 μm. A part of the studied samples was subjected to the uniaxial stretch deformation for the purpose of studying specific features of the structural transforma-

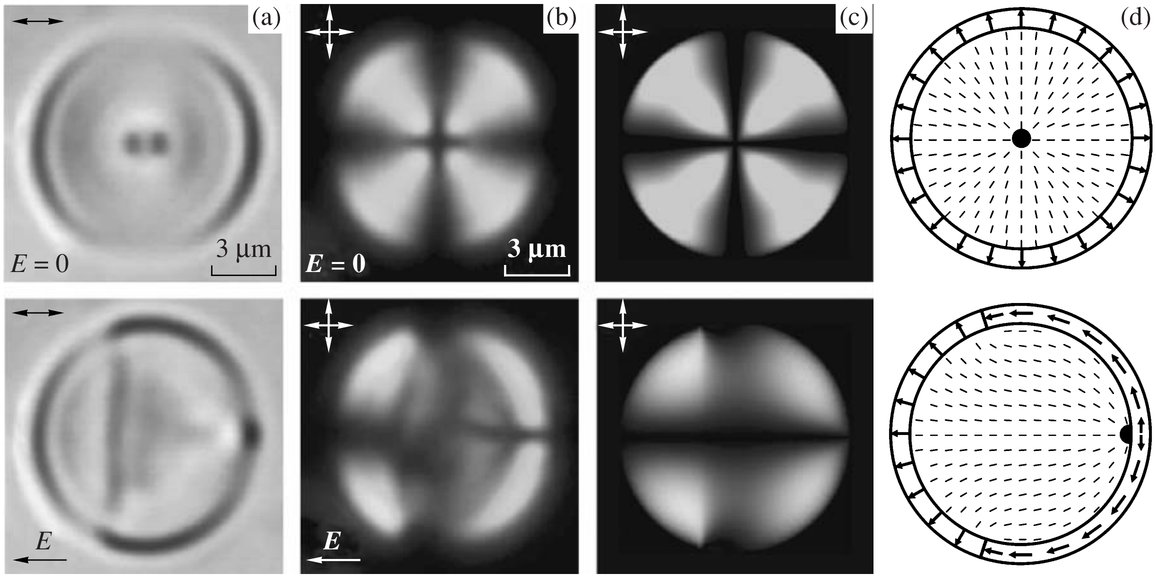

Fig. 1. Transformation of (upper row) the radial director configuration under the action of a dc electric field into (lower row) the structure containing boojum and ring-shaped surface defect. Photographs of nematic droplets (a) with a switched-off analyzer and (b) in crossed polarizers. (d) Calculated director configurations in LC and (c) the corresponding droplet textures in crossed polarizers. (a–c) Double arrows indicate the orientation of the polarizers. (d) Arrows in the droplet shell show the topology used in the calculations of the director field at the droplet surface.

tions in prolate droplets. The textural patterns of the droplets were observed using a polarizing optical POLAM P-113 microscope and photographed by a digital photographic camera in the geometry of crossed polarizers and also with a switched-off analyzer. For the materials used, the ordinary component $n_{\perp lc}$ of the LC refractive index is approximately equal to the polymer refractive index n_p. This is convenient for analyzing the director orientation at the interface between the nematic and polymer. In the case of a switched-off analyzer, the droplet boundary is virtually unseen in the regions where light is polarized perpendicular to the director. And vice versa, due to the strong light scattering, the interface is clearly seen as a dark line in the regions where the director is parallel with the light polarization.

The experimental studies were accompanied by the numerical calculations of the director configurations in the LC droplets and the corresponding textural patterns. The orientational structures were calculated by the well-known method of minimizing the energy of elastic distortions of the director field in the bulk of the LC [9]. This method was adapted to the study of ellipsoid-shaped droplets with the inhomogeneous boundary conditions [10, 11]. The contribution of the external electric field to the LC alignment in the bulk was not taken into account, because, at a high concentration of ionic addition, the field of spatially separated ion charges almost fully blocks the action of the external field [12]. The droplet shape and the boundary conditions were taken in accordance with the experimental data. The textural patterns of LC droplets in the crossed polarizers were calculated using the theoretical model [13].

RESULTS AND DISCUSSION

In all of the studied samples of the composite films, the radial structure (Figs. 1–3, upper row) with the bulk defect-hedgehog [14] in the droplet center was initially formed. The typical textural pattern of the droplet in the crossed polarizers has the geometry of a Maltese cross. This implies that the used concentration of homeotropic surfactant will suffice to form a nanosized CTA^+ layer over the entire surface blocking the tangential orienting effect of the polymer matrix.

The corresponding scheme of the director distribution in the bulk of the droplets (Figs. 1d–3d, upper rows where the central section parallel to the film plane is shown for the droplet) and their textural patterns (Figs. 1c–3c, upper rows) can be calculated using the condition of the homogeneous homeotropic director alignment over the entire droplet surface. In some droplets, the extinction bands are bent (Fig. 3b, upper row), indicating that the director lines are twisted. In this case, a small chirality of the nematic structure must be taken into account in the computational procedure.

The textural patterns change drastically under the action of an electric field (Figs. 1–3, lower rows). In this case, the observed changes can proceed following three various scenarios that ultimately result in the formation of three hitherto unknown structures, whose specifics is determined by the azimuthal director distribution in the surface region with tangential anchoring.

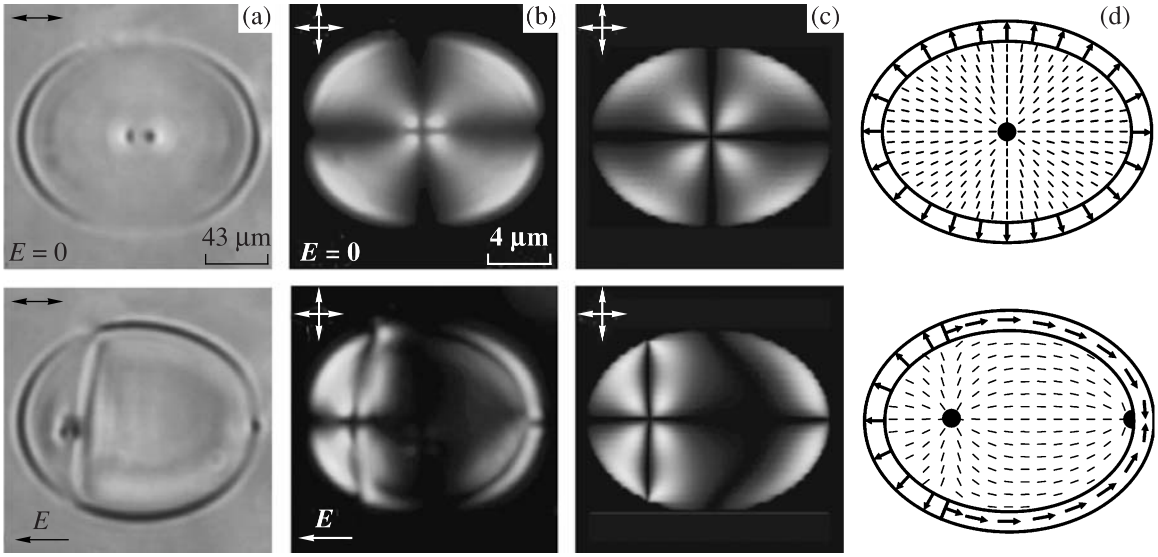

Fig. 2. Transformation of (upper row) the radial configuration into (lower row) the structure containing a hedgehog, boojum, and ring-shaped surface defect. Photograph positions, computational data, and designations are as in Fig. 1.

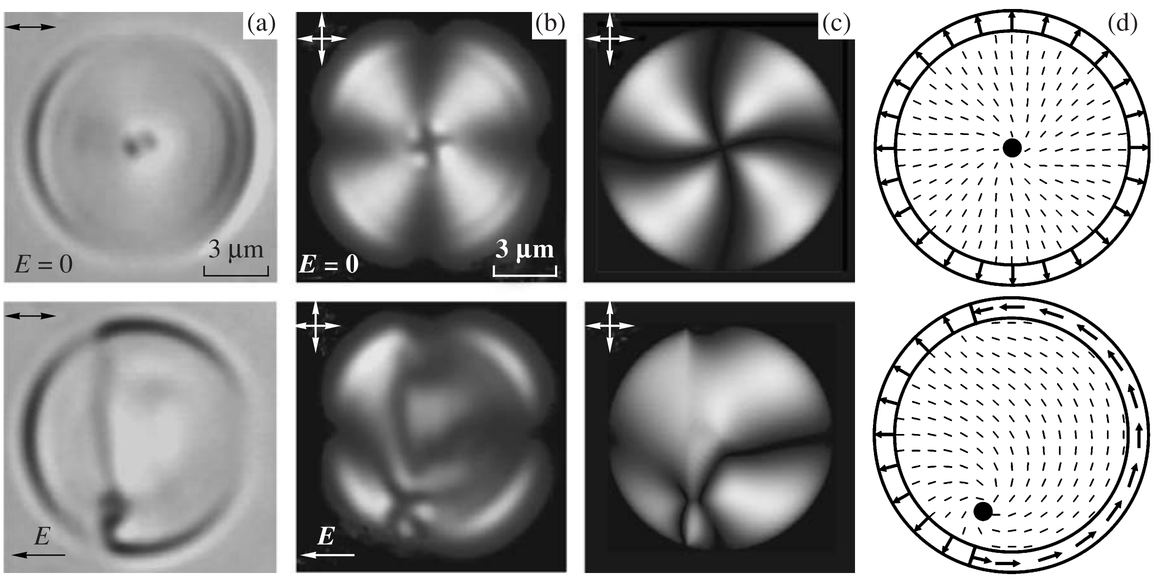

Fig. 3. Transformation of (upper row) the radial configuration into (lower row) the structure containing a hedgehog and ring-shaped surface defect. Photograph positions, computational data, and designations are as in Fig. 1.

1. *Transition of the Radial Configuration to the Structure Containing Surface Point Defect (Boojum) [14] and Linear Ring-Closed Surface Disclination (Fig. 1, lower row).* In this case, a small region of tangential anchoring surrounded by a region with a smooth transition of the director orientation from tangential to homeotropic is initially formed on the right side of the surface. A point surface defect with the strength $m = -1/2$ is formed at the center of the region with tangential anchoring [15]. Unlike a boojum [14], the director lines do not enter this defect and deflect from it along the trajectories close to the hyperbola. Then, the region with the tangential director alignment expands, while the hedgehog moves from the droplet center to the formed surface defect and merges with it. As a result, boojum arises at the surface to play the role of a source for the director field. Then, the tangential anchoring occupies more than half the droplet surface. The edges

of this region are situated where a dark line corresponding to the strong light scattering terminates abruptly at the droplet boundary in the upper and lower parts of the photograph (Fig. 1a, lower row). Two regions with different director orientations on the polymer wall are separated by a surface defect in the form of a ring perpendicular to the film plane (it is seen in Fig. 1a as a dark vertical line to the left of the droplet center). The structure described above can form in the spherical droplets, although it arises with the greater probability in the prolate droplets if the electric field is directed perpendicular to their long axis.

The resulting director distribution can be modeled using the appropriate boundary conditions (Fig. 1d, lower row). It should be emphasized that, in this case, the director must emerge from the boojum in different directions, according to its role as the source. One can see (Fig. 1c, lower row) that the droplet texture obtained using the calculated configuration coincides in the outline with the experimental pattern (Fig. 1b, lower row), confirming that the analysis presented above is correct.

2. *Transition of the Radial Configuration to the Structure Containing a Hedgehog, Boojum, and Surface Ring-Shaped Defect (Fig. 2, lower row).* This transformation occurs most frequently in the prolate droplets if the electric field is directed along their long axis. At the beginning of the process, boojum arises on the right side of the surface. Near the boojum, a ring-shaped surface defect forms at the interface between the tangential and homeotropic anchoring, whereupon it gradually moves to the left half of the droplet. The hedgehog shifts to the plane of the ring-shaped defect. This completes the structural transformation. It is noteworthy that boojum plays the role of a drain in this case, and this should be taken into account when modeling the configuration. That is, the director field in the region of tangential surface anchoring must converge at the boojum on all sides (Fig. 2d, lower row), making the calculated pattern (Fig. 2c, lower row) consistent with the experiment (Fig. 2b, lower row).

3. *Transition of the Radial Configuration to the Structure Containing a Hedgehog and Ring-Shaped Surface Defect (Fig. 3, lower row).* This process proceeds in a qualitatively different way most frequently in the radial droplets with the originally twisted director lines. In this structure, a ring-shaped surface disclination also appears at the interface between the tangential and homeotropic anchoring. The hedgehog moves from the droplet center to the plane of the ring-shaped defect and shifts to the surface to stop short of reaching it. Analysis of the photographs indicates that the defect-free nearly homogeneous director distribution is formed in the tangential surface zone. In our calculations, we attempted to take into account this fact by specifying the counterclockwise director direction at the surface for all droplet sections parallel to the central section shown in Fig. 3d in the lower row. Although the resulting texture (Fig. 3c, lower row) does not fully coincide with the experimental pattern (Fig. 3b, lower row), the main features (hedgehog position, direction of extinction bands emerging from hedgehog) are in agreement with each other.

All of the processes described above are reversible. It should be emphasized that all three variants of the structural transition, which differ in the director azimuthal distribution in the surface region with tangential anchoring, can occur in the same spherical droplet and under the same experimental conditions. The reasons for which one or another transformation scenario is realized calling for further investigations. It is likely that the deciding role in these systems is played by the thermal fluctuations producing certain distortions of the radial structure at the instant the field is switched on. However, it is shown above that, by varying the parameters of the material or the experimental conditions, one can strongly shift the balance between the probabilities of these processes.

CONCLUSIONS

A characteristic distinction between the two ways of implementing the electrically controlled ionic modification of the interface is as follows. *In the normal regime of the effect [6], the initial alignment of the LC is determined by the polymer matrix*, while the electric field induces the formation of a ~10-nm layer of surface-active ions in the respective region of the droplet surface, thereby blocking the orienting effect of the polymer. In [6], the initial tangential LC alignment was changed in a local region of the interface to the homeotropic alignment inherent in the used surfactant. However, the reverse reconstruction of the boundary conditions is also possible, e.g., for a composite of homeotropically orienting polymer and ionic surfactant with the tangential anchoring.

In the inverse regime considered in this work, the initial structure of the LC droplets is governed by the nanosized layer of the surface-active ions, which covers the entire interface because of a high surfactant concentration. Under the action of an electric field, ions leave the corresponding surface region where the boundary conditions characterizing a polymer matrix are regained. By choosing various combinations of the orienting abilities of the polymer and surfactant, one can implement other variants in the reconstruction of the boundary conditions and, correspondingly, various scenarios of the orientational and structural transformations. Moreover, our study has shown that the resulting director configurations and, hence, the optical properties of the PDLC films are quite sensitive to some material and the structural parameters of the medium, such as the surfactant concentration, LC chirality, droplet anisometry, etc.

It should be emphasized that the ionic surfactant method can be used to control not only the LC dispersions. Our preliminary studies have shown that this approach is also efficient in porous and lamellar LC materials.

It follows from this work that the detailed studies of the effect of the electrically controlled ionic modification of surface anchoring and the corresponding orientational and structural transformations in various LC media, as well as the development of new functional materials for optoelectronics and nanophotonics are highly topical.

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